Microwave Plasma-Assisted Chemical Vapor Deposition of Conductive Carbon Coatings on Cathode Active Materials for Li-ion Batteries

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$LiFePO_4$ is an attractive material for use as a potentially low-cost, environmentally benign, and safe alternative to $LiCoO_2$ cathode materials for rechargeable lithium batteries [1,2].However, poor rate capability of $LiFePO_4$ that has been attributed to low electronic conductivity and/or slow diffusion of lithium ions across the two-phase boundary, makes it difficult to utilize $LiFePO_4$ electrodes fully in lithium cells at room temperature. To address these issues, synthesis techniques have been optimized to minimize particle size [3,4,5], improve the conductivity by doping [6], addition of metal or carbon particles during synthesis [7], reactive ball-milling of $LiFePO_4$ with carbon [8] or co-synthesis of conductive carbon coatings on the particles during pyrolysis of organic additives [9,10].

On the other hand, conductive carbon black additives are commonly used in almost all Li-ion composite electrodes to increase cycle life and decrease polarization of the electrode. A conductive carbon matrix that provides good electronic contact between oxide particles and the current collector is essential for good electrochemical performance of composite electrodes. However, even small amounts of carbon additive result in lower volumetric energy density of composite electrodes [11]. So that neither energy nor power density are unduly compromised, it is imperative to optimize carefully the carbon quality, content and distribution in composite electrodes.

The quality of carbon coating proved particularly important in enhancing utilization and rate capability of $LiFePO_4$ cathodes [12,13]. These improved electrochemical properties are mainly associated with the structural and electronic properties of a co-synthesized carbon coating. The larger the ratio of sp^2-coordinated carbon (excellent electronic conductor) to disordered or sp^3-coordinated carbonaceous materials (poor electronic conductors), the better electrochemical utilization of $LiFePO_4$. However, the *in situ* carbon coating of $LiFePO_4$ by simple pyrolysis ($T<800^oC$) of organic precursors cannot produce graphite-like conductive carbon.

Microwave irradiation offers a clean, inexpensive, and convenient method of material synthesis, which can result in higher yields and shorter reaction times. Microwave plasma assisted chemical vapor deposition (MPACVD) Microwave plasma technique is now widely used for an industrial scale thin-film deposition e.g., metal oxides, diamond. The objective of this work was to use MPACVD to produce highly conductive graphitic coatings on cathode active material powders.

Thin layers of different organic precursors were microwaved in low-pressure Ar plasma at 300-1000 W for 5 s to 3 min. Interaction of organic precursors with low-pressure Ar-plasma and strong electromagnetic radiation led to rapid pyrolysis of organic compounds at relatively low temperatures. Vaporization of the organic precursor and subsequent rapid pyrolysis yielded uniform films of nanometer-sized carbon particles. Low-pressure microwave induced plasma synthesis of graphitic carbon on $LiFePO_4$ powder produced thin carbon films directly on the active material. The structure and morphology of carbon thin films were examined using Raman spectroscopy, SEM and TEM.

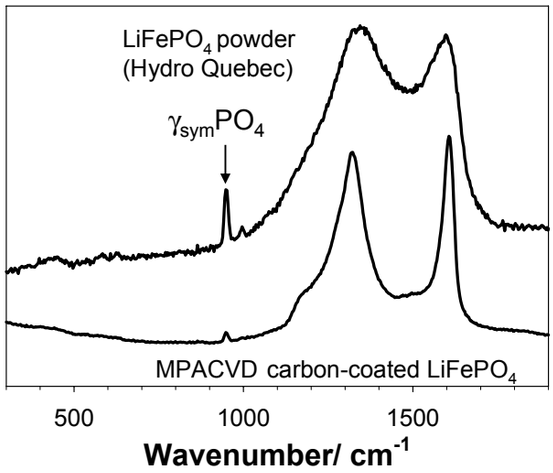

Figure 1. Raman spectra of pristine $LiFePO_4$ and MPACVD carbon-coated .$LiFePO_4$.

The produced carbon films consisted of densely packed ~50 nm large primary particles. The structure of microwaved carbon was highly crystalline with consistent graphene domain size. Carbon coatings exhibited high sp^2-graphene crystalline structure, and excellent electronic conductivity is expected. Electrochemical performance of carbon-coated $LiFePO_4$ will be presented.

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